

Calculation of the basic kinetic parameters of thermo-oxidative degradation of polyethylene and its copper-containing composites

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Abstract

Calculation of the basic kinetic parameters of thermo-oxidative destruction of initial, porous HDPE and copper-containing composites based on porous HDPE was carried out by the IKP method. It was shown that thermo-oxidation of these materials consisted of three stages: (1) the migration of oxygen molecules to the active oxidising centres and the beginning of chain oxidation; (2) destruction of polymer molecules; and (3) thermodegradation of “nuclei”. However, porous HDPE was oxidised at lower temperature. Thermooxidation of copper-containing porous HDPE composite was characterised by the higher activation energy. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Solvent crazing [1] is a process of the transition of glassy and semicrystalline polymers in a highly dispersed and oriented state by the uniaxial deformation in the adsorptionally active media (e.g. alcohol, amines). Modification of polymers by solvent crazing leads to changes of the polymer structure and physico-mechanical parameters and to the appearance of pores. These porous polymer matrices can be used as templated membranes for obtaining polymer-inorganic composites, e.g. copper-containing composites [2]. The fibrillar-porous structure of the polymer allows one to localize the nucleation sites of the inorganic phase.

The objective of this work was to show the influences of porous structure prepared via solvent crazing and small addition of highly disperse copper particles on HDPE thermo-oxidation. In the first place, a study of a thermo-oxidative degradation of polymers is very important for understanding the polymer modification mechanism in crazing. Thus, the amount of the oxidizing centres and the activation energy of oxygen diffusion to the oxidizing centres can be changed by changes of

initial polymer structure. Secondly, an influence of copper particles on the thermo-oxidative processes of PE was shown in [3] to be equivocal: copper could accelerate or retarded PE oxidation.

The possibility of use of mathematical methods for calculation of the kinetic parameters of high-temperature pyrolysis of crazed, porous polypropylene films was shown earlier [4]. The basic methods of kinetic parameter calculation [5,6] are based on the modification of the fundamental kinetic equation:

$$d\alpha/dt = k^*f(\alpha) \quad (1)$$

where α is the degree of conversion.

But these methods demand exact expression of the function $f(\alpha)$. For example, in other work [5] the reaction rate is suggested to be proportional to the concentration of polymer links:

$$f(\alpha) = (1 - \alpha)^n \quad (2)$$

the simplest type of $f(\alpha)$ as a function for first-order reaction being usually used. However, thermo-oxidation of polymers is a complicated multi-stage process with elimination of gaseous products. Such processes are described by some mechanisms (nucleation and nucleus

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growing, diffusion of different orders and others) so the kinetic of these processes cannot be described by one of the standard functions $f(\alpha)$ (Table 1) of the most probable mechanism.

The method of the invariant kinetic parameters (IKP) is used in this work [7]. Not only kinetic parameters of thermo-oxidative destruction but also probabilities for the degradation functions can be found by the IKP method. Data obtained are independent of the experimental conditions and no assumption is made concerning the kinetic degradation function.

The IKP method is based on use of the integral Arrhenius equation

$$\log\left(\frac{g_j(\alpha_{iv})}{T_{iv}^2}\right) = \log\left(\frac{A_{jv}R}{\beta_v E_{jv}}\right) - \frac{E_{jv}}{2.3RT_{iv}}, \quad (3)$$

$$g_j(\alpha) = \int_0^\alpha \frac{d\alpha}{f_j(\alpha)},$$

where A_j and E_j are activation energies and pre-exponential factors, respectively, β_v are linear heating rates. The basic suggestion of the method is the fulfilment of a compensation effect [8]. A compensation effect of this kind is classified as false or as superficial resulting from parameter distortion by an inappropriate kinetic model function. For each function $f_j(\alpha)$, $\log A_j$ versus E_j is plotted and if a compensation effect is observed, a linear relation is observed for each heating rate β_v and defined by the equation:

$$\log A_{jv} = B_v + l_v E_{jv},$$

where $B = \log(k)$ (a constant of the reaction rate), and $l = 1/(2.3RT)$ for each heating rate.

Using independent kinetic parameters E_{inv} and $\log A_{inv}$, a kinetic equation appropriate to the most probable mechanism of a process can be found by the formula (4):

$$\bar{S}_j = \frac{1}{p} \sum_{v=1}^{v=p} S_{jv}, \quad (4)$$

where

$$(n-1)S_{jv}^2 = \sum_{i=1}^{i=n} \left| \left(\frac{d\alpha}{dt} \right)_{iv} \frac{A_{inv}}{\beta_v} \exp\left(\frac{-E_{inv}}{RT_{iv}}\right) f_j(\alpha) \right|^2,$$

where S is the residual sum of squares for each $f(\alpha)$ and each heating rate, and p is a function of heating rates.

2. Experimental

To obtain a porous matrix of the polymers and composite materials we used a 75- μm film made of industrial-grade isotactic high-density polyethylene (HDPE) as the initial material. To be transformed into a highly dispersed oriented state, HDPE was deformed in isopropanol until the desired degrees of stretching (200%). Creation and evolution of polymer porous structure passed through delocalized crazing [1]. The porous structure was stabilised in the isometric conditions by a thermal treatment to 120 °C for 3 h. The size of the pores was no more than 6.5 nm.

Copper-containing HDPE samples were obtained by the thermochemical method described previously [2].

The structure of the as-received samples was studied by SEM. The test samples were prepared using brittle fracture in liquid nitrogen and decorated with a platinum-palladium alloy. All SEM studies were performed on a Hitachi S-520 scanning electron microscope.

The TG analyses were performed using a Mettler-TG50 at five heating rates β_v (10, 15, 20, 30 and 50 °C/min) from 25 to 600 °C under air. The samples (about

Table 1
Kinetic models used in the IKP method

Kinetic models	$f_i(\alpha)$	$g_i(\alpha)$		
Nucleation and nucleus growing	$1/n(1-\alpha)[- \ln(1-\alpha)]^{1-n}$	$[- \ln(1-\alpha)]^n$	S1- $n=1/4$	
			S2- $n=1/3$	
			S3- $n=1/2$	
			S4- $n=2/3$	
			S5- $n=1$	
Phase boundary Reaction	$(1-\alpha)^n$	$1-(1-\alpha)$	S6	
			$2[1-(1-\alpha)^{1/2}]$	S7
			$3[1-(1-\alpha)^{1/3}]$	S8
Diffusion	$1/2\alpha^{-1}[- \ln(1-\alpha)]^{-1}$ $3/2[(1-\alpha)^{-1/3}-1]^{-1}$	α^2	S9	
			$(1-\alpha)\ln(1-\alpha)+\alpha$	S10
Potential law	$1/n \alpha^{1-n}$	$1-2/3 \alpha-(1-\alpha)^{2/3}$	S11	
			$\alpha^n (0 < n < 2)$	S12- $n=1/4$
				S13- $n=1/3$
				S14- $n=1/2$
				S15- $n=2/3$
Reaction order	$1/n(1-\alpha)^{1-n}$	$1-(1-\alpha)^{1/2}$	S16- $n=3/4$	
			$1-(1-\alpha)^{1/3}$	S17- $n=1/2$
				S18- $n=1/3$

10^{-5} kg) were placed in an open clay crucible. Precision of temperature measurements was ± 1.5 °C.

Calculation of the basic kinetic parameters of thermo-oxidative destruction of initial (HDPE), porous (PE-200) polyethylene and copper-containing composite based on PE-200 [CM-200 (Cu)] was carried out by the IKP method [7] using an Excel program.

3. Results and discussion

The integral (a) and differential (b) TG curves of the initial, porous and copper-containing HDPE are presented in Fig. 1. The initial HDPE loses a mass in a single peak in 380–480 °C with maximum of the loss rate at 380 °C. PE-200 loses a mass by wide double peak in 250–550 °C with small loss rate in all temperature intervals. CM-200 (Cu) loses a mass by double peak in 310–510 °C with maximum of the loss rate at 420 °C. Thus, creation of the pore system and the introduction

of copper particles influence the degradation of HDPE in different ways. It is shown that the HDPE thermo-oxidation is accelerated when the porosity grows, irrespective of the fact that the working temperature is more than 350 °C and HDPE is melted. But introduction of the finely-dispersed copper particles in the porous polymer matrices retarded the thermo-oxidative processes.

These facts can be connected with structure of porous and copper-containing HDPE (Fig. 2). The structure of PE-200 is seen in Fig. 2(a) to be a system of co-penetrated pores connected by fibrils, so the amount of the oxidizing centres is increased and activation energy of the diffusion of oxygen molecules to the oxidizing centres is decreased.

The composite is a blend with a high level of mutual dispersion of the polymer and copper; filler particles with sizes 80–200 nm are spherically shaped and are located at the walls of microvoids and fibrils [Fig. 2(b)]. Therefore, the copper particles were oxidised at the beginning and they protected HDPE matrices from degradation.

The curves of mass loss versus temperature built by model kinetic functions are non-linear curves which can be divided into three basic linear parts with different

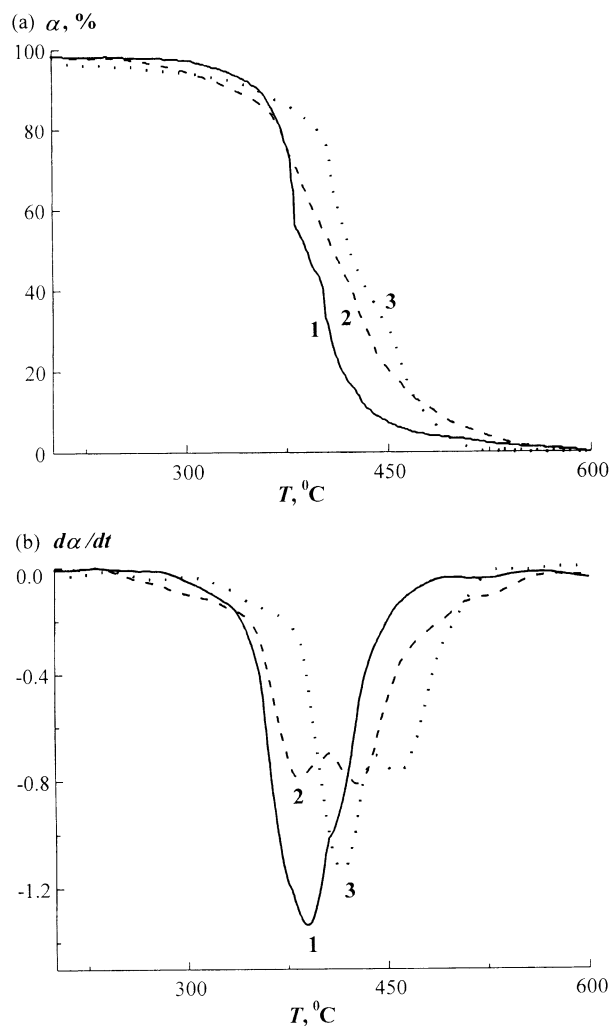


Fig. 1. TG (a) and DTG (b) curves of the initial HDPE (1), PE-200 (2) and CM-200 (Cu) (3).

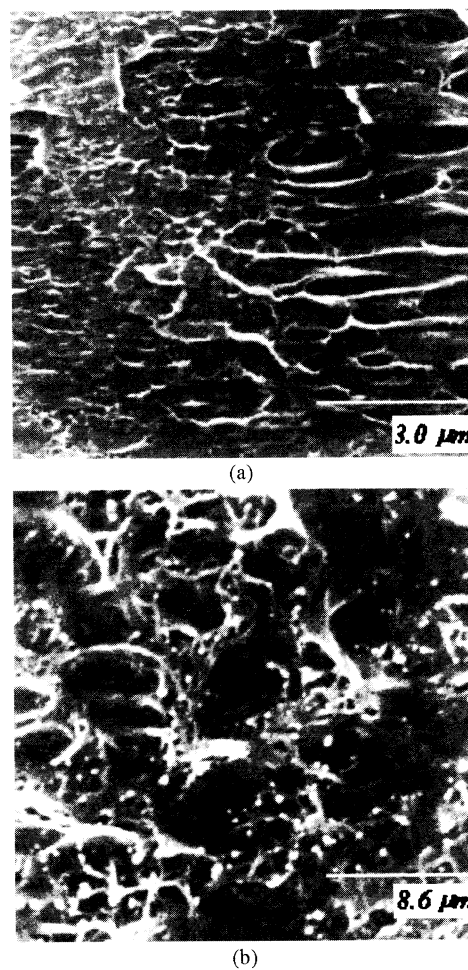


Fig. 2. SEM images of PE-200 (a) and CM-200 (Cu) (b).

slopes relative to the abscissa for all samples. An example of such a model curve in half-logarithmic coordinates is presented in Fig. 3. This type of curve is proof of a three-stage mechanism of thermo-oxidative degradation of polyethylene. The temperature intervals of the stages are approximately identical irrespective of samples. Namely, the first stage was carried out in a temperature interval from 250 to 380 °C, the second stage from 400 to 450 °C and the third stage from 450 to 490 °C. Every stage was approximated by a linear function with good precision ($R^2=0.97\text{--}0.99$) and then pairs ($\log A_{jv}$; E_{jv}) were found.

The compensation effect is observed for each heating rate and material (Fig. 4). The values of k_v at temperature T_v are then calculated from the slopes of the straight lines with $R^2=0.96\text{--}0.99$.

E_{inv} and $\log A_{inv}$ found for every temperature intervals and literature data for comparison are presented in

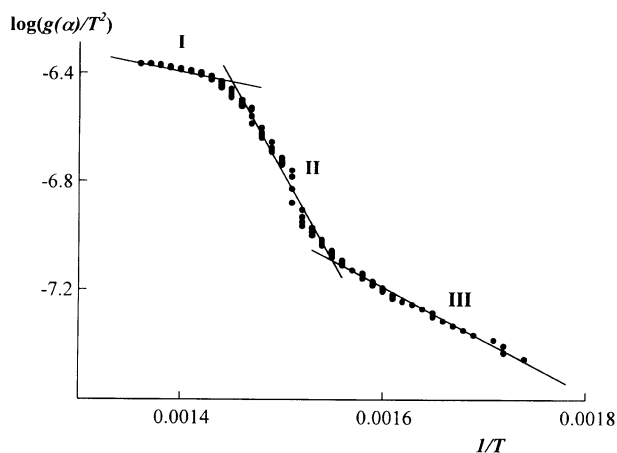


Fig. 3. Typical example of the dependence of logarithmic kinetic function of S12 model mechanism from square of reverse temperature for CM-200 (Cu).

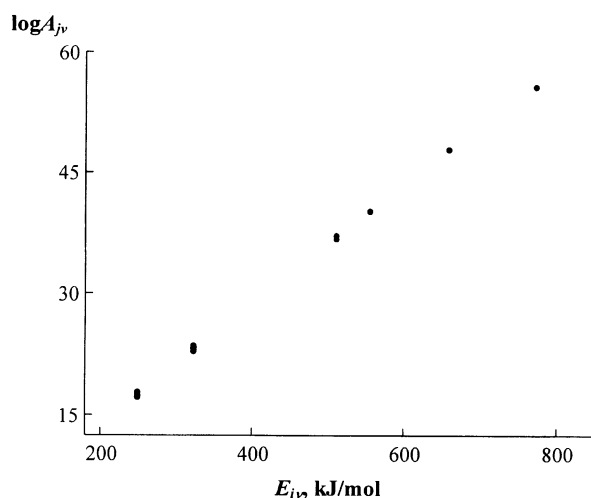


Fig. 4. Example of observed compensation effect between apparent activation energy and pre-exponential factor (PE-200; heating rate 10 °C/min).

Table 2. Calculated kinetic parameters are shown to be comparable with literature data [3], and a similarity of behaviour of initial HDPE and porous PE-200 and their distinction to thermo-oxidation of copper-containing composite CM-200 (Cu) can be stressed. Copper particles change ratios of basic stage rates of degradation and so the thermal stability of copper-containing composite is higher than non-filled HDPE.

For a thorough study of peculiarities of HDPE thermo-oxidative degradation the probabilities of model mechanisms for I–III temperature intervals were found by a mathematical statistic method. Basic thermo-oxidative mechanisms for three temperature intervals are presented in Fig. 5(a)–(c) for I–III, respectively.

Basic process determining rate in I temperature interval (Fig. 5a) is diffusion (S9, S10 mechanisms). Copper-containing composite obtained by thermal reduction contains some low-molecular products that can be oxidized at 220–380 °C, but the polymer matrix is not degraded. The initial HDPE and PE-200 are not oxidized at the same temperature. The summarized probability of diffusion mechanisms for CM-200 (Cu) is 60%. Processes of potential law mechanisms (S12, S13) are 15% and processes of nucleating mechanisms (Si, S2) are 8%: Si and S2 mechanisms point out a creation of chain oxidation on the active centres, and Si 2 and Si 3 show the development of a polymer chain degradation.

The processes of polymer chain degradation were carried out at about 400 °C (II temperature interval) which was supported by histograms (Fig. 5b). This stage is seen to fit by potential laws of different orders (S12, S13). Non-filled matrices, in contrast to copper-containing composites, are characterised by a great contribution of diffusion mechanisms. Oxygen molecules penetrate inside amorphous region of initial HDPE and pores of PE-200

Table 2

Invariant kinetic parameters of HDPE samples obtained by IKP method

Sample	Temperature interval (°C)	E_{inv} (kJ/mol)	$\log A_{inv}$
<i>I</i>			
HDPE	280–400	–	–
PE-200	290–400	–	–
CM-200 (Cu)	220–350	92±18	5.4±1.1
<i>II</i>			
HDPE	400–430	160±15	11.0±1.0
PE-200	420–450	165±16	11.3±1.1
CM-200 (Cu)	380–490	222±20	16.0±2.0
LDPE ([3])	~400	100	–
HDPE ([3])	~400	150	–
<i>III</i>			
HDPE	440–490	40±5	1.6±0.2
PE-200	470–490	57±20	2.8±0.9
CM-200 (Cu)	> 500	–	–

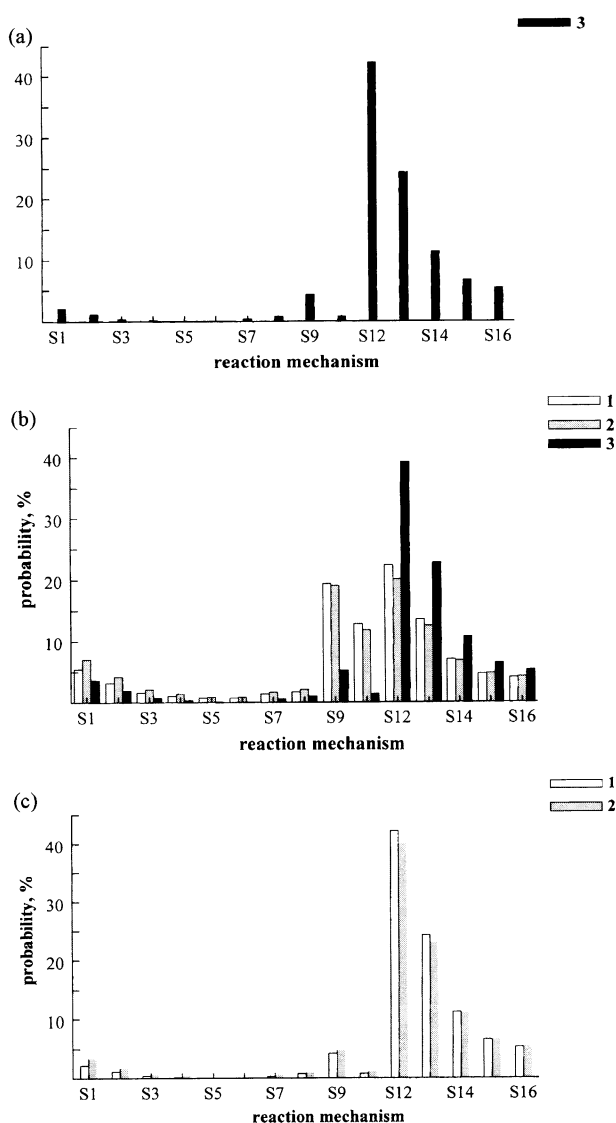


Fig. 5. Histograms of probabilities of block HDPE (row 1), PE-200 (row 2) and CM-200 (Cu) (row 3) thermo-oxidative degradation in I (a), II (b) and III (c) temperature intervals.

where oxidizing kinetic chain begins to develop only at a high temperature. No nucleating mechanisms are important for CM-200 (Cu) at the second temperature interval. Also, the activation energy of the composite is higher than for block and porous PE, which is connected with the presence of low-molecular organic filler in the pores of polymer matrices.

The stage of a degradation of a “nucleus” (it is difficult to access places in polymer) was carried out at 470–500 °C (III temperature interval). The third stage (Fig. 5c) is described by potential laws (S14–S14) too

and is characterised by lower activation energy than second stage.

4. Conclusions

The IKP method was shown in the present work to be useful for the calculation of the thermo-oxidation kinetic parameters of the solvent-crazed porous and copper-containing HDPE.

To summarise, the theoretical calculations supported an experimental suggestion [9] that the thermo-oxidative degradation of HDPE could be formally divided into three stages: a creation of chaining oxidative process (S1 and S9 mechanisms), thermo-oxidation of macromolecules and thermodestruction of the “nucleus” (S12 and S13).

However, porous HDPE was oxidised at lower temperature and in a wider temperature range. This fact was connected with the increased amount of the oxidizing centres and decreased activation energy of the diffusion of oxygen molecules to the oxidizing centres when the porosity was formed.

Thermooxidation of copper-containing porous HDPE composite was carried out through the same stages but at the higher temperature and was characterised by the higher activation energy.

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